

Ab-initio procedure for effective models of correlated materials with entangled band structure

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Abstract

We present a first-principles method for deriving effective low-energy models of electrons in solids having entangled band structure. The procedure starts with dividing the Hilbert space into two subspaces, the low-energy part (“ d space”) and the rest of the space (“ r space”). The low-energy model is constructed for the d space by eliminating the degrees of freedom of the r space. The thus derived model contains the strength of electron correlation expressed by a partially screened Coulomb interaction, calculated in the constrained random-phase-approximation (cRPA) where screening channels within the d space, P_d , are subtracted. One conceptual problem of this established downfolding method is that for entangled bands it is not clear how to cut out the d space and how to distinguish P_d from the total polarization. Here, we propose a simple procedure to overcome this difficulty. In our scheme, the d subspace is cut out from the Hilbert space of the Kohn Sham eigenfunctions with the help of a procedure to construct a localized Wannier basis. The r subspace is constructed as the complementary space orthogonal to the d subspace. After this disentanglement, P_d becomes well defined. Using the disentangled bands, the effective parameters are uniquely determined in the cRPA. The method is successfully applied to 3d transition metals.

I. INTRODUCTION

In the last several decades many new materials with intriguing properties were discovered and synthesized. These materials range from the high-temperature superconductors to magnetic materials, and the latter have already found real applications in electronic industry. Typically, most of these materials contain elements from the $3d$ or $4f$ rows and their electronic structure is characterized by the presence of a partially filled narrow band across the Fermi level. The fact that the narrow band is partially filled implies that there are many configurations with approximately equal weight rendering a one-particle description of the electronic structure problematic. Indeed, it has been recognized for a long time that many of the intriguing properties of these materials originate from correlations among the electrons residing in the partially filled narrow band. The electrons are neither fully localized, like core electrons, nor itinerant, like s or p electrons in alkalis or conventional semiconductors such as silicon or diamond. This hybrid property poses a tremendous theoretical difficulty for an accurate description of the electronic structure, because due to the electrons' partially itinerant character the problem can neither be treated as a purely atomic problem nor within a pure band picture. Moreover, the interaction with other electrons can be very important.

A large amount of work has been directed to solving the correlation problem of the above materials. The usual approach is to consider only the narrow bands near the Fermi level and eliminate the degrees of freedom for the rest of the bands by the downfolding procedure, resulting in the well-known Hubbard model which contains an effective on-site Coulomb interaction, the Hubbard U . In general, the models represent multi-band systems containing interorbital as well as long-ranged part of Coulomb interaction. The models can then be solved with various sophisticated low-energy solvers such as dynamical mean-field theory (DMFT) [1] or solvers for lattice models [2].

An important issue in mapping the real system to a model Hamiltonian is how to determine the one-particle kinetic energy term and the effective interaction or the Hubbard U in the model. Unlike the one-particle parameters that can be downfolded from the band structure, the Hubbard U is much more elusive to determine and it is often treated as an adjustable parameter. A widely used scheme to calculate the Hubbard U from first-principles is the constrained LDA (cLDA) method [3, 4, 5]. The cLDA method, however, is known from early on to yield values of U , which are too large in some cases (e.g. late transition

metals). It has been argued that this arises from technical difficulty in including transitions of electrons between the d and r space contributing the screening processes. This oversight leads in some cases to a larger value of U [6]. Recent extensions of the cLDA method may be found in Refs.[7] and [8]. Another method for determining the effective interaction is a scheme based on the random phase approximation (RPA). Early attempts along this direction can be found in Refs.[9, 10]. A combined cLDA and RPA method to circumvent the difficulty was also proposed [11].

Some years ago a scheme for calculating the Hubbard U , called the constrained RPA (cRPA) scheme [12], was proposed. The main merit of the cRPA method over currently available methods is that it allows for a precise elimination of screening channels, which are instead to be included in a more sophisticated treatment of the model Hamiltonian. This is a controlled approximation without any ambiguity, expected to become asymptotically exact if the r -space becomes well separated from the d space. Moreover, the effective screened interaction can be calculated as a function of \mathbf{r} and \mathbf{r}' , i.e., $U(\mathbf{r}, \mathbf{r}')$, independent of the basis functions. This allows easy access to obtaining not only on-site matrix elements but also off-site matrix elements as well as screened exchange matrix elements, which are usually taken to be the atomic value. Another merit is the possibility of obtaining the frequency-dependent Hubbard U , which may prove to be important. The cRPA method has now been applied to a number of systems with success [6, 13, 14, 15].

Although the cRPA method is rather general, its applications to real systems have revealed a serious technical problem. The problem arises when the narrow band is entangled with other bands, i.e., it is not completely isolated from the rest of the bands. In many materials, the narrow band of interest is entangled. Even in simple materials such as the $3d$ transition metals, the $3d$ bands mix with the $4s$ and $4p$ bands. Similarly, the $4f$ bands of the $4f$ metals hybridize with the more extended s and p bands. For such cases, it is not clear anymore which part of the polarization should be eliminated when calculating the Hubbard U using the cRPA method.

Some procedures to overcome the problem of determining U for entangled bands have been attempted. One of these is to choose a set of band indices and define the bands of Hubbard model as those bands corresponding to the chosen indices. Another alternative is to introduce an energy window and define the Hubbard bands to be those that have energy within the energy window. Yet another alternative is to have a combination of energy

window and band indices. These procedures, however, suffer from a number of difficulties. When choosing band indices it is inevitable that some of the states will have a character very different from that of the intended model. For example, in the case of $3d$ transition metals, choosing five “ $3d$ ” bands will include at some \mathbf{k} -points states which have little $3d$ character, with a considerable $4s$ component instead. Moreover, the chosen bands will be awkward to model since they do not form smoothly connected bands. A similar problem is encountered when choosing an energy window. A combination of band indices and energy window proposed in Ref. [6] partially solves the problem but it suffers from arbitrariness. Another procedure is, as we will discuss in detail later, to project the polarization to the orbitals of interest, e.g., $3d$ orbitals, but this procedure has been found to yield an unphysical result of negative static U . In this work, we offer a solution to the problem of determining the Hubbard U for entangled bands. The basic idea is to disentangle the narrow bands of interest from the rest and carry out the cRPA calculation for the disentangled band structure, not using the original band structure. The disentangling procedure is described in Sec.II. We apply the method to $3d$ transition metals in Sec.III and show that the method is numerically stable and yields reasonable values of U . Finally the paper is summarized in Sec.IV.

II. METHOD

In the cRPA method we first choose a one-particle subspace $\{\psi_d\}$, which defines the model Hamiltonian, and label the rest of the Hilbert space by $\{\psi_r\}$. We define P_d to be the polarization within the d subspace and the total polarization is written as P . It is important to realize that the rest of the polarization $P_r = P - P_d$ is *not* the same as the polarization of the r subspace because it contains polarization arising from transitions between the d and r subspaces. Since P_d is the polarization of the model Hamiltonian, this polarization should be subtracted out from the total polarization when the effective parameter of the model is determined. The effective Coulomb interaction W_r should be calculated with the rest of the polarization P_r :

$$W_r(\omega) = [1 - vP_r(\omega)]^{-1}v, \quad (1)$$

where v is the bare Coulomb interaction. It can indeed be shown [12] that the fully screened interaction is given by

$$W = [1 - W_r P_d]^{-1} W_r . \quad (2)$$

This mathematical identity ensures that W_r can be interpreted as the effective interaction among the electrons residing in the d subspace since the screening of W_r by P_d leads to the fully screened interaction. The matrix elements of W_r in some localized functions can then be regarded as the frequency-dependent Hubbard U . It has been shown that the formula in Eq.(1) is formally exact, provided P_r is the difference between the exact polarization P and the exact polarization of the d subspace P_d . In the cRPA method, P_r is calculated within the random-phase approximation.

If the d subspace forms an isolated set of bands, as for example in the case of the t_{2g} bands in SrVO_3 , the cRPA method can be straightforwardly applied. However, in practical applications, the d subspace may not always be readily identified. An example of these is provided by the $3d$ transition metal series where the $3d$ bands, which are usually taken to be the d subspace, do not form an isolated set of bands but rather they are entangled with the $4s$ and $4p$ bands. To handle these cases we propose the following procedure.

We first construct a set of localized Wannier orbitals from a given set of bands defined within a certain energy window. These Wannier orbitals may be generated by following the post-processing procedure of Souza, Marzari and Vanderbilt [16, 17] or other methods, such as the preprocessing scheme proposed by Andersen *et al.* within the Nth-order muffin-tin orbital (NMT0) method [18]. We then choose this set of Wannier orbitals as the generators of the d subspace and use them as a basis for diagonalizing the one-particle Hamiltonian, which is usually the Kohn-Sham Hamiltonian in the local density approximation (LDA) or generalized gradient approximation (GGA). The so obtained set of bands, which equivalently define the d subspace, may be slightly different from the original bands defined within the chosen energy window, because hybridization effects between the d and r spaces are neglected. However, it is important to confirm that the dispersions near the Fermi level well reproduces the original Kohn-Sham bands. From these bands we calculate the polarization \tilde{P}_d as

$$\tilde{P}_d(\mathbf{r}, \mathbf{r}'; \omega) = \sum_i^{\text{occ}} \sum_j^{\text{unocc}} \left[\frac{\tilde{\psi}_i^*(\mathbf{r}) \tilde{\psi}_j(\mathbf{r}) \tilde{\psi}_j^*(\mathbf{r}') \tilde{\psi}_i(\mathbf{r}')}{\omega - \tilde{\varepsilon}_j + \tilde{\varepsilon}_i + i\eta} - \frac{\tilde{\psi}_i(\mathbf{r}) \tilde{\psi}_j^*(\mathbf{r}) \tilde{\psi}_j(\mathbf{r}') \tilde{\psi}_i^*(\mathbf{r}')}{\omega + \tilde{\varepsilon}_j - \tilde{\varepsilon}_i - i\eta} \right], \quad (3)$$

where $\{\tilde{\psi}_i\}$, $\{\tilde{\varepsilon}_i\}$ ($i = 1, \dots, N_d$) are the wavefunctions and eigenvalues obtained from diagonalizing the one-particle Hamiltonian in the Wannier basis.

It would seem sensible to define the rest of the polarization as $P_r = P - \tilde{P}_d$, where P is the full polarization calculated using the *original* (Kohn-Sham) wavefunctions and eigenvalues $\{\psi_i\}$, $\{\varepsilon_i\}$ ($i = 1, \dots, N$), and calculate W_r according to Eq.(1). We have found, however, that this procedure is numerically very unstable, resulting in some cases to unphysically negative static U and a large oscillation as a function of frequency. This is understandable given that P and \tilde{P}_d are obtained from two different band structures, so that low energy screening channels associated with the d - d transitions are not excluded from P_r completely. Due to the singular nature of the expression in Eq.(1) these low-energy excitations can cause a large fluctuation in W_r .

Another way of calculating P_r is to project the wavefunctions to the d space,

$$|\bar{\psi}_i\rangle = \hat{\mathcal{P}}|\psi_i\rangle, \quad (4)$$

where the projection operator $\hat{\mathcal{P}}$ is defined as

$$\hat{\mathcal{P}} = \sum_{j=1}^{N_d} |\tilde{\psi}_j\rangle \langle \tilde{\psi}_j|. \quad (5)$$

The effective d polarization may be expressed as

$$\bar{P}_d(\mathbf{r}, \mathbf{r}'; \omega) = \sum_i^{\text{occ}} \sum_j^{\text{unocc}} \left[\frac{\bar{\psi}_i^*(\mathbf{r}) \bar{\psi}_j(\mathbf{r}) \bar{\psi}_j^*(\mathbf{r}') \bar{\psi}_i(\mathbf{r}')}{\omega - \varepsilon_j + \varepsilon_i + i\eta} - \frac{\bar{\psi}_i(\mathbf{r}) \bar{\psi}_j^*(\mathbf{r}) \bar{\psi}_j(\mathbf{r}') \bar{\psi}_i^*(\mathbf{r}')}{\omega + \varepsilon_j - \varepsilon_i - i\eta} \right], \quad (6)$$

and $P_r = P - \bar{P}_d$ can be used to calculate W_r . We found that this procedure does not work either and is again unstable. This problem may be related to the fact that $\bar{\psi}_i$'s are not orthogonal with each other and transitions between the states do not correspond to single particle-hole excitations.

Based on these observations we propose the following procedure. We define the r subspace by

$$|\phi_i\rangle = (1 - \hat{\mathcal{P}})|\psi_i\rangle \quad (7)$$

which is orthogonal to the d subspace constructed from the Wannier orbitals. In practice it is convenient to orthonormalize $\{\phi_i\}$ and prepare $N - N_d$ basis functions. By diagonalizing the Hamiltonian in this subspace a new set of wavefunctions $\{\tilde{\phi}_i\}$ and eigenvalues $\{\tilde{\epsilon}_i\}$ ($i = 1, \dots, N - N_d$) are obtained. As a consequence of orthogonalizing $\{\tilde{\phi}_i\}$ and $\{\tilde{\psi}_j\}$, the set of r bands $\{\tilde{\epsilon}_i\}$ are completely disentangled from those of the d space $\{\tilde{\epsilon}_j\}$, and they are slightly different from the original band structure $\{\epsilon_i\}$. As we will see later, however, the numerical tests show that the disentangled band structure is close to the original one.

The Hubbard U is calculated according to Eq.(1) with $P_r = \tilde{P} - \tilde{P}_d$, where \tilde{P} is the full polarization calculated for the *disentangled* band structure. It is important to realize that the screening processes between the d space and the r space are included in U , although the d - r coupling is cut off in the construction of the wavefunctions and eigenvalues.

III. RESULTS AND DISCUSSIONS

As an illustration we apply the method to 3d transition metals. The electronic structure calculations are done in the local density approximation [19] of density functional theory [20] with the full-potential LMTO implementation [21]. The wavefunctions are expanded by *spdf* + *spd* MTOs and a $8 \times 8 \times 8$ \mathbf{k} -mesh is used for the Brillouin zone summation. Spin polarization is neglected. More technical details are found elsewhere [13, 22].

Figure 1(a) shows the Kohn-Sham band structure of nickel. There are five orbitals having strong 3d character at [-5 eV:1 eV], crossed by a dispersive state which is of mainly 4s character. Using the maximally localized Wannier function prescription with the energy window of [-7 eV:3 eV], interpolated “ d ” bands are obtained. The subsequent disentangling procedure gives the associated “ r ” bands. Comparing Fig.1(b) with (a) we can see that there is no anti-crossing between the d bands and the r bands in (b). Otherwise the two band structures are nearly identical.

In order to see the impact of the disentanglement on the screening effects, we perform the full RPA calculation using the disentangled band structure. The fully screened Coulomb interaction is compared with that for the original band structure in Fig.2 where the average of the five diagonal terms in the Wannier basis φ_i is plotted,

$$W(\omega) = \frac{1}{5} \sum_{i=1}^5 \int d\mathbf{r} d\mathbf{r}' \varphi_i^*(\mathbf{r}) \varphi_i(\mathbf{r}) W(\mathbf{r}, \mathbf{r}'; \omega) \varphi_i^*(\mathbf{r}') \varphi_i(\mathbf{r}') . \quad (8)$$

The two methods yield similar results. The static values agree with each other within 0.2 eV, and the frequency dependence is weak at low frequencies. As frequency increases there is a sharp increase at ~ 20 eV, where screening by plasmons becomes ineffective. These results assure that screening effects can be treated accurately with the disentangled band structure.

The Hubbard U is calculated by the constrained RPA, namely, by replacing W in Eq.(8) with W_r . The results are shown in Fig.3. There is no large fluctuation against frequency, in contrast to the methods described in Sec.II, and $U(\omega)$ shows a stable behavior. As is expected, U is significantly larger than W at low frequencies. This implies proper elimination of $d-d$ screening processes is crucial. Comparing with the previous results using a combined energy and band window [13], the agreement is reasonably good. A small difference between these two results at low frequency may be due to a small portion of $d-d$ screening presumably contained in the previous method [13], although it should be excluded from the cRPA calculations.

We carried out the calculations for a series of other 3d metals as well and found in all the cases that (i) the present scheme is numerically stable and does not result in unphysical frequency dependence of U , and (ii) the value of $W(\omega)$ is close to that from the original band structure. The latter is confirmed in Fig.4 where the static values ($\omega \rightarrow 0$ limit) are summarized. Concerning U , the present method gives larger values compared to the previous results, particularly for early transition metals. Since W is nearly equal to each other in the two methods, the discrepancy is ascribed to the different treatment between P_d and \tilde{P}_d . We should note that P_d in the previous method depends on the choice of the window. For a wider window, obviously we would obtain a better agreement. Also, some states have a mixed character of 3d and 4s near the anti-crossing points. This makes elimination of the screening process difficult in the original band structure. The present scheme, on the other hand, enables us to determine U without ambiguity. The d bands are disentangled from the r bands. Consequently, the polarization in the d space is well-defined and can be removed completely in $P_r = \tilde{P} - \tilde{P}_d$.

In the present formulation, small off-diagonal matrix elements of the Kohn-Sham Hamiltonian between the d space wavefunction $|\psi_i\rangle$ constructed from the Wannier orbitals and the

r space $|\phi_j\rangle$ are ignored. This is the reason why the anti-crossing is avoided. If the energy of this hybridization point in the band dispersion is smaller than the screened Coulomb energy and the energy scale of the interest, strictly speaking, one has to keep all of these hybridizing bands in the effective model, because the hybridization effects are non-perturbative. In the present case of transition metals, the energy crossing point of $4s$ and $3d$ bands are relatively larger than the screened Coulomb energy scale and the low energy models constructed only from the $3d$ Wannier orbitals may give at least qualitatively reasonable description of the low energy physics.

IV. SUMMARY

We have proposed a method to calculate the effective interaction parameters for the effective low-energy models of real materials when bands are entangled. The key point is to first properly orthogonalize the low-energy subspace contained in the models and the complementary high-energy subspace to each other. This orthogonalization by the projection technique enables the disentanglement of the bands. Once the disentangled band structure is obtained, the constraint RPA method can be used to determine the partially screened Coulomb interaction uniquely. Numerical tests for $3d$ metals show that the method is stable and yields reasonable results. The method is applicable to any system. Applications to more complicated systems, such as interfaces of transition metal oxides are now under way.

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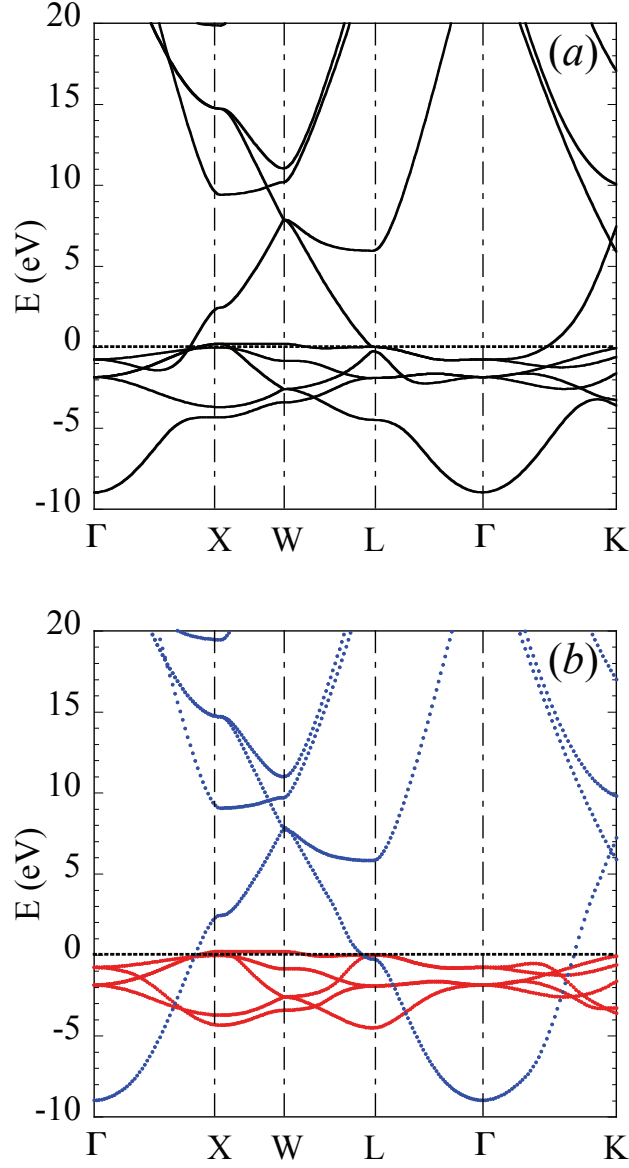


FIG. 1: (Color) (a) Kohn-Sham band structure of nickel in the LDA. (b) Disentangled band structure with d - r hybridization switched off. The red lines show the d states obtained by the maximally localized Wannier scheme, while the blue lines are disentangled r states. Energy is measured from the Fermi level.

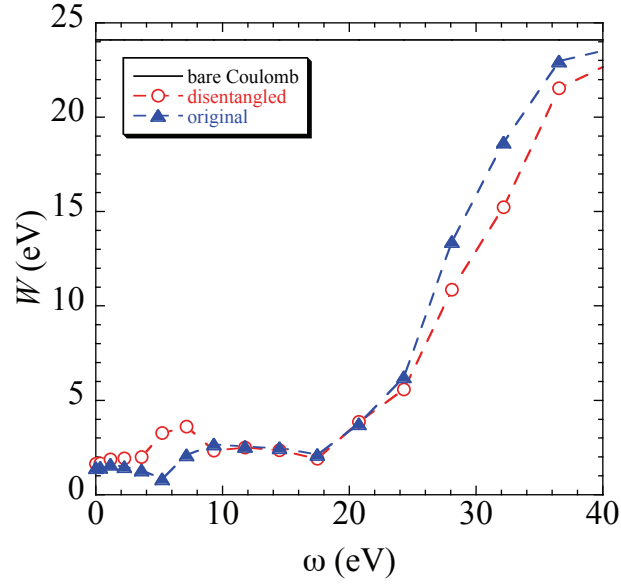


FIG. 2: (Color online) Fully screened Coulomb interaction of nickel as a function of frequency. The average of the diagonal terms in the Wannier basis is plotted. The present scheme using the disentangled bands is compared to the results from the original band structure.

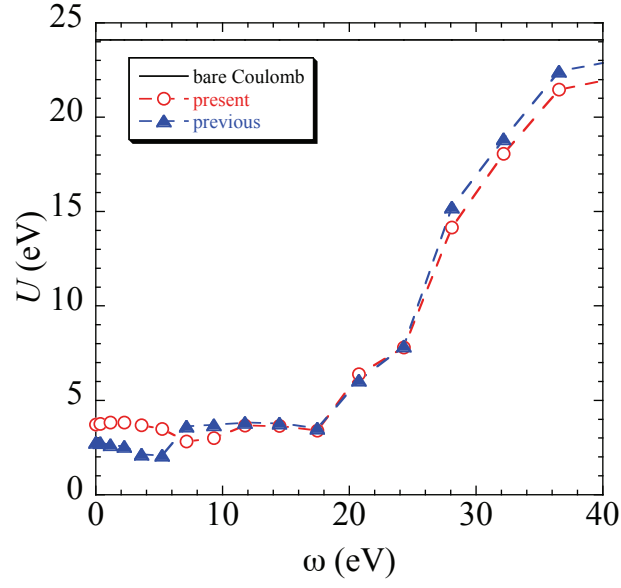


FIG. 3: (Color online) Hubbard U of nickel as a function of frequency. The diagonal term of the partially screened interaction in the Wannier basis is calculated by the present method and compared with the published data of Ref.[13].

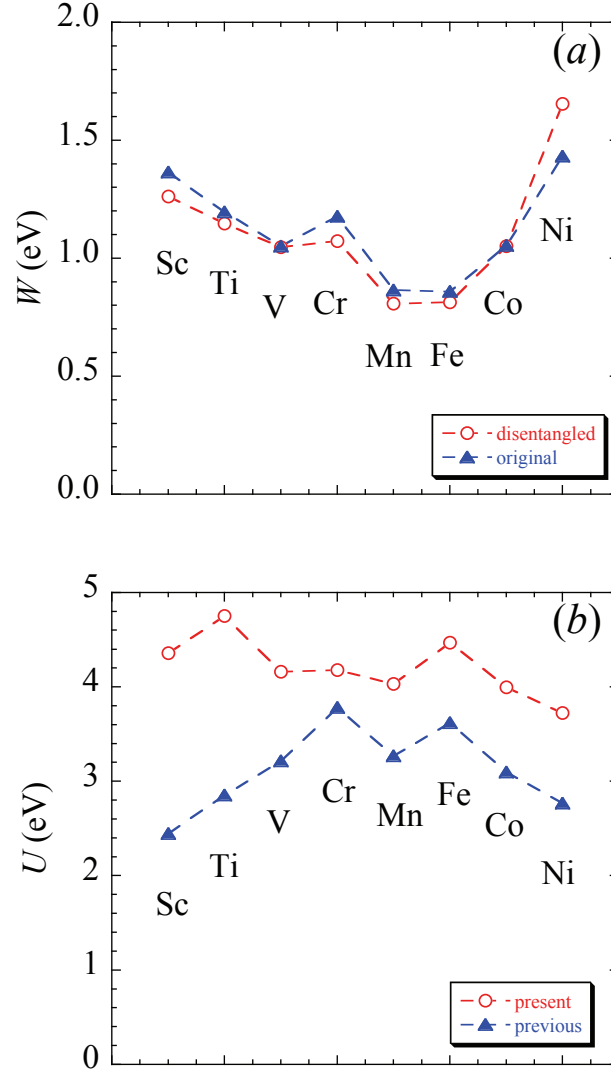


FIG. 4: (Color online) Static values of (a) fully screened Coulomb interaction W and (b) Hubbard U for 3d metals.